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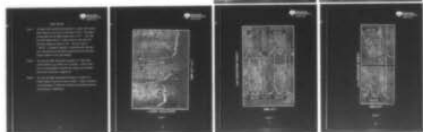
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RAMAN SCATTERING STUDIES OF THE GAAS NATIVE OXIDE INTERFACE.(U)
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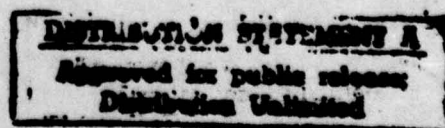
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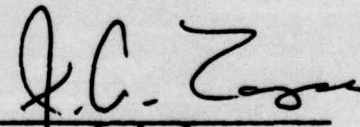


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Oxide films grown by heat treatment on the 100 and 111 faces of GaAs have been studied by Raman backscattering. A spectrum consisting of the bulk LO and TO lines of GaAs and two additional lines labeled R1 and R2 is observed on all samples prepared at temperatures above 435°C. The additional modes are attributed to an interface region of perhaps several hundred angstroms thickness beneath the oxide film.		

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This structure appears to be made unstable by chemical removal of the film. After the film is removed, the spectrum is annealed (returns to that of GaAs) in a matter of weeks at room temperature and in about one hour at 400°C whether the annealing atmosphere is N₂, O₂, or forming gas. One of the modes, R2, appears to scatter as a scalar, i.e., a diagonal Raman matrix element. Spectra scattered by the R1 mode on the other hand appear to be largely unpolarized and slightly nondiagonal in character. Some speculations about the possible composition and structure of the interface region are presented.

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I. INTRODUCTION

In the pursuit of a better understanding of the physics of surfaces and interfaces, new experimental tools are needed with which to complement the already impressive list of techniques developed in recent years. Excellent methods, for example, have been developed, for determining the chemical species and their compositional profile in surface layers. Raman scattering offers potential insight into the structure, dynamics, and dielectric properties of surface and interface regions, information which may be complementary to that offered by other techniques.

We have reported elsewhere¹ on the study of PbTe-SnTe alloy surfaces by Raman scattering. Evidence was presented for the observation of vibrational modes of single crystal surface adsorbate as thin as 1-2 atomic layers. In the following we report studies on native oxide films on GaAs.

Oxide films were grown on GaAs platelets by heating in pure oxygen between 435°C and 710°C. These exhibited a Raman spectrum which is attributed to a thick (perhaps several hundred angstroms) transition region between the oxide and the GaAs substrate.

II. EXPERIMENTAL

The GaAs samples, in the form of polished wafers, were, with few exceptions, undoped (i.e., typically $\rho > 3000 \Omega \text{ cm}$) GaAs prepared by Crystal Specialties, Inc., Monrovia, California. In some instances, Cr-doped specimens were used with no detectable difference in results. Oxidation was carried out by heating in the presence of flowing high purity oxygen after carefully cleaning the wafer surface.²

At 400°C, no evidence of oxide either visually or by Raman scattering was evident on a (100) face after several hours³. At 435°C a layer "golden brown" in color and judged to be 200-300Å in thickness was grown in seven hours.³ Various films all exhibiting interference colors and all probably substantially thicker than the latter were grown on (100) faces for various times at various temperatures up to 710°C. Oxidation of a (111) face appeared to be significantly slower. For example, a specimen heated for 30 min at 495° exhibited no obvious coloration visually.

Conventional Raman "backscattering" spectra were obtained at room temperature using an argon-ion laser at 0.5145 and 0.4880 μ and a double monochromator equipped with holographic gratings. The partially focused laser beam was at near normal incidence (15°) to the surface and light scattered normal to the surface was collected with approximately f/10 optics.

Figure 1 shows the characteristic Raman spectrum exhibited by the thermally oxidized samples. The peak labeled L0 shifted 293 cm^{-1} from the exciting laser line is light scattered by the bulk longitudinal optical phonon of the GaAs substrate. Scattering from the L0 mode is "allowed" in [100] backscattering but not from the bulk transverse (T0) phonon at 267 cm^{-1} . Apparently a small amount of transverse optic mode (T0) scattering was induced as a result of the oxidation procedure (the T0 peak height for the majority of the samples was relatively smaller than that of Fig. 1). The peaks labeled R1 and R2 are new. We argue, in the following, that they originate from a transition region at the interface between the transparent oxide film and the underlying GaAs.

III. RESULTS

1) All of the samples heated in oxygen between 435° and 710°C exhibited spectra similar to that of Fig. 1. The peak R2 was generally about twice as strong as R1 and varied from approximately the same intensity as the L0 peak in some samples to perhaps 3-4 times as strong as the L0 peak in others. No correlation between peak height and growth time or temperature has been deduced thus far.

2) The oxide film could be removed readily by etching for a few minutes in HCl at 55°C. The resultant surface was alike in appearance, visually, to unoxidized GaAs. However, the Raman spectrum - apart from some reduction in the elastic scattering background which accompanies the removal of the oxide film - appeared to be nearly unchanged or reduced at most by small fraction. With the further passage of time the interface modes R1 and R2 appeared to decrease slowly. Thus far, we have found that the only etchants which remove the R1 and R2 peaks also attack the GaAs substrate.

3) The (111) faces of GaAs exhibit spectra altogether similar to that of Fig. 1 when oxidized thermally, though the oxidation appears to be substantially slower as mentioned above. Again, as in the case of (100) faces, the oxide film is easily removed in HCl leaving a surface with the appearance of GaAs, but a sensibly unaltered Raman spectrum.

4) Information on the symmetry properties of the scattering modes can be inferred from polarization experiments. Some of our results are shown in Fig. 2 for light backscattered from a (100) face and in Fig. 3 from a (111) face. For brevity we use the notation (x,y) where x and y are the polarization directions of the incident and scattered light,



respectively. The data indicate that the scattering peaks occurring at the bulk LO and TO mode frequencies obey the selection rules of the GaAs structure⁴ (space group T_d^2). In each case the mode R2 appears to favor (x,x) scattering and to be relatively forbidden in (x,y) configurations (the intensity scale is logarithmic so that the polarization ratios are greater than they appear to be). Thus, R2 is the result of scalar scattering or a diagonal Raman tensor component. The scattering at R1 on the other hand, appears to vary relatively little with polarization and if anything favors (x,y) scattering over (x,x).

5) The interface structure appears to be "stable" in the respect that no discernable change in the Raman spectrum has been detected for our oldest samples (several months at this writing). However, after the oxide film is chemically removed, the Raman lines R1 and R2, which are initially nearly unchanged as mentioned above, begin to decrease and in some samples have disappeared in less than one month at room temperature in air. In addition we find that if an etched sample is placed in either dry nitrogen, forming gas (96% N₂ 4% H₂), or oxygen and heated to about 400°C for about 1 hour, the two lines are completely removed leaving a clean GaAs spectrum. (In some cases, a weak TO line is retained for the [100] samples). In contrast, a sample for which the film had not been removed when heated at 675°C in forming gas for 10 minutes, did not show any signs of change.

6) XPS (x-ray photoelectron spectroscopy) yields information on the chemical composition of the first few atom layers of a solid. A film grown at 675°C showed a Ga:As ratio of more than 10:1. This result is in agreement with the findings of several other workers.^{5,6} Shortly after

chemical removal of the oxide film, a sample oxidized at 690°C showed an As:Ga ratio of ~5:1 at the newly exposed surface. Some oxygen was also present, but the sample had been exposed to air for a few hours. After the R1 and R2 lines had disappeared as a result of room temperature annealing for 4 weeks, an XPS scan of the "same" surface showed an As:Ga ratio of about 3. Small lines were attributable to As and Ga as oxide, but the principal peaks appeared to correspond to As and Ga as gallium arsenide. The presence of excess As at the interface is in disagreement with the conclusions of Sealy and Hemment.⁵

IV. DISCUSSION

The most significant features of the interface modes R1 and R2 are 1) they are generally at least as intense as the bulk phonon lines of GaAs and 2) they are sufficiently narrow as to suggest a well-defined energy. The results of the last section appear to be consistent with the possibility that these lines arise from an interfacial layer between the easily removed oxide and the substrate GaAs. This suggestion is in agreement with the speculations of Zaininger and Revesz⁷ who proposed that thermal oxides on GaAs might have a "composite" structure with an arsenic rich interface region. The XPS data on the etched surface support this view. The possibility of an arsenic rich interface has been discussed also by Schwartz,⁶ but is in disagreement with the conclusions of Sealy and Hemment.⁵

The strong intensity of the interface Raman lines suggests that the interface region is at least one hundred angstroms thick and may be a good deal more.⁸ On the other hand, we observe 1) that the T0 and L0 peaks appear to obey the bulk GaAs selection rules, 2) their intensity

is less than that of bulk GaAs when the interface lines are present, but increases as the interface lines anneal out, and 3) the weak line (Fig. 2) at $\sim 160 \text{ cm}^{-1}$ is often seen also on clean GaAs and is believed to correspond to two phonon $[2TA(X)]$ of bulk GaAs. These results suggest that some of the light is penetrating to the pure GaAs substrate material. This would limit the interface layer to not more than perhaps 1000\AA .

Apparently, the interface layer and the oxide film form a stable combination possibly because of electrostatic forces at the interface. It seems necessary to conclude that when the oxide film is removed, the surface region gradually reverts to GaAs, possibly by diffusion of Ga vacancies or by evaporation of excess arsenic. In any event it seems not to be by surface reaction because of the insensitivity of the process to the gas ambient.

In addition to establishing the composition of the interface region, it is necessary to establish the atomic arrangement before the properties of these surface layers can be understood. It seems unlikely to us that the intensity and sharpness of the observed spectra can be attributed to a large continuously graded region in which the gallium vacancy level is never sufficiently great as to restructure the medium. It is possible in such a structure that one or both of the interface modes might arise from normally forbidden first order processes or from enhanced second order processes. For example, R2 corresponds quite well to expected values for the transverse optic mode frequency at either the X point or the L point of the Brillouin zone. To explain the strong scattering, however, it would be necessary to assume a strong perturbation, e.g., a large strain field, throughout the sizable scattering region. We know of no instances



in which comparable effects have been observed. On the other hand, a truly amorphous region seems unlikely. Such a medium should scatter in a scalar fashion, i.e., without altering the polarization of the incident light. The mode R2 is of this type, but R1 is clearly not. If the layer were quite polycrystalline on the other hand, the scattered light might be expected to be largely unpolarized. The mode R2 is certainly not unpolarized. R1, on the other hand, might fit this description, but the polarization data suggest that there is some degree of order in the interface region. It may be that the transition region is in effect two layers; a region epitaxial to the GaAs (for example, a tetragonal structure could scatter like the R1 mode) followed by a nearly amorphous region adjacent to the oxide film. Obviously, more work is needed to clarify these matters.

ACKNOWLEDGMENTS

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1. J. A. Cape, L. G. Hale and W. E. Tennant, Surface Science, in press.
2. The samples were successively rinsed in 5:1:1 $\text{H}_2\text{O}/\text{Na}_3\text{OH}/\text{H}_2\text{O}_2$ (50°C), 5:1:1 $\text{H}_2\text{O}/\text{HCl}/\text{H}_2\text{O}_2$ (50°C), and pure HCl (50°C), for about one minute each, then rinsed in flowing H_2O .
3. No appreciable growth below 400°C has also been reported by K. Navrátil, Czech. J. Phys. B18, 266 (1968).
4. In [100] backscattering, T0 scattering is forbidden, while the L0 mode scatters [010] components into [001] and vice versa. See R. Loudon, Advances in Physics 13, 423 (1964). In many of our samples a small amount of T0 scattering seems to have been induced by the oxidation process. It is not unusual to see some T0 backscattering from [100] surfaces probably because of imperfections in the surface region.
5. Several authors have noted the preponderant gallium content of the oxide. H. J. Minden, J. Electrochem. Soc. 104, 733 (1962), reported electron diffraction studies which indicated that oxide films grown above 600°C were $\beta\text{-Ga}_2\text{O}_3$. See also, B. J. Sealy and P.L.F. Hemment, Thin Solid Films 22, S39 (1974).
6. B. Schwartz, CRC Critical Reviews in Solid State Sciences 5 (4), 609 (1975), has given a review of GaAs surface oxides.
7. K. H. Zaininger and A. G. Revesz, J. Phys. Paris, 25, 208 (1964).
8. The penetration depth of 0.5μ light into GaAs is about 1000Å. Since the etched surface looks remarkably like GaAs, we assume the optical constants of the surface layers are similar to GaAs and we assume that the Raman cross section is not greatly different than that of GaAs. On this basis a comparable Raman intensity suggests a comparable depth.

FIGURE CAPTIONS

- Figure 1 The Raman [100] backscattering spectrum of a GaAs (100) surface after heating in pure O_2 for 20 minutes at $710^\circ C$. The numbers at each peak give the Raman energy shift in cm^{-1} . The lines R1 and R2 remain after all visible traces of the oxide film have been removed by etching in HCl. The small peak at $\sim 160\text{ cm}^{-1}$ is frequently observed in backscattering from GaAs and is believed to be two phonon scattering by bulk transverse acoustic phonons at the zone boundary.
- Figure 2 The polarized Raman backscattering spectra of a GaAs (100) surface heated in O_2 at $675^\circ C$ for 15 minutes. Crystal directions in the parenthesis indicate the incoming and scattered polarization directions, respectively.
- Figure 3 The polarized Raman backscattering spectra of a GaAs (111) surface heated in O_2 one half hour at $560^\circ C$. Crystal directions in the parenthesis indicate the incoming and scattered polarization directions, respectively.

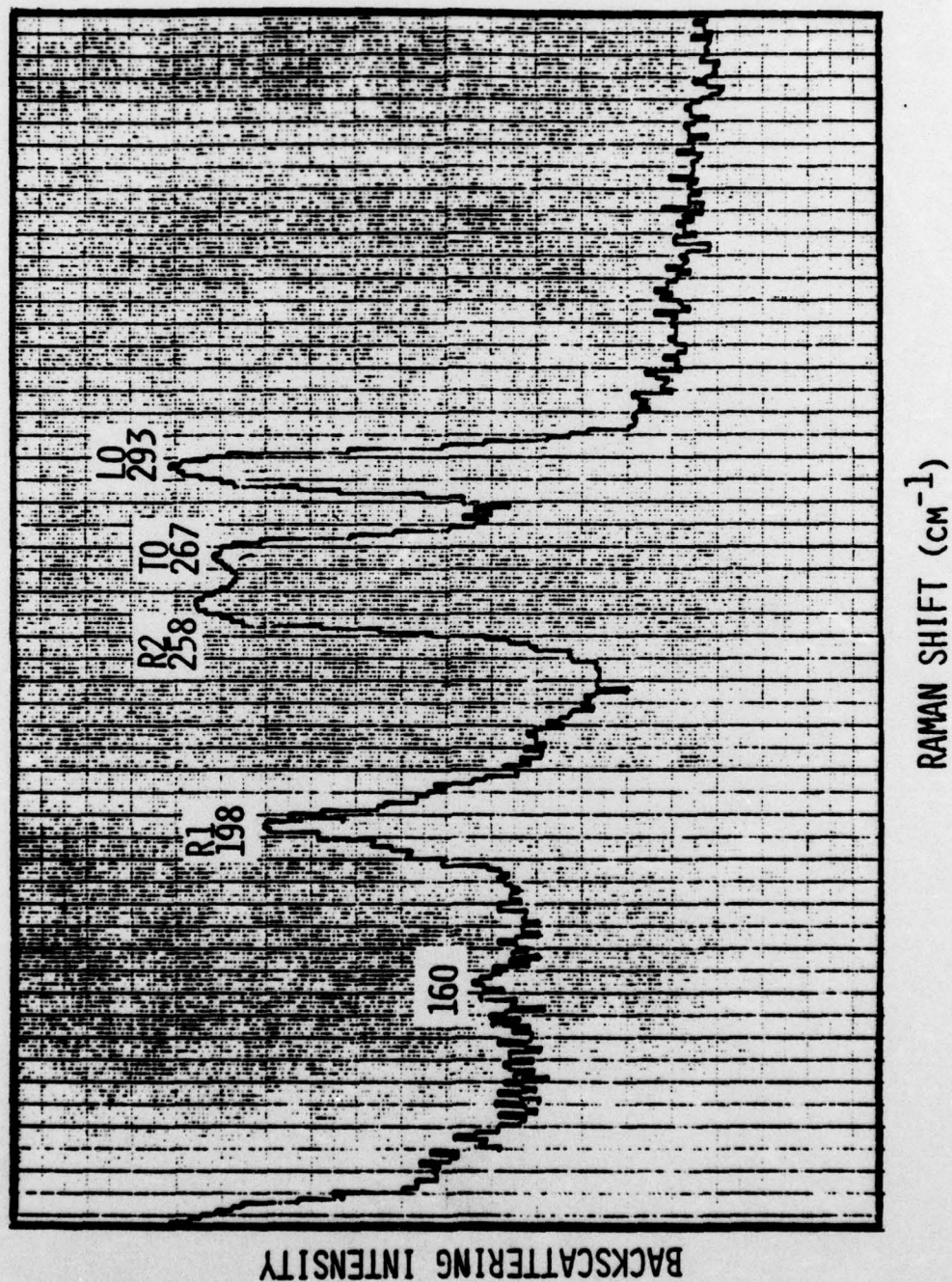


Figure 1

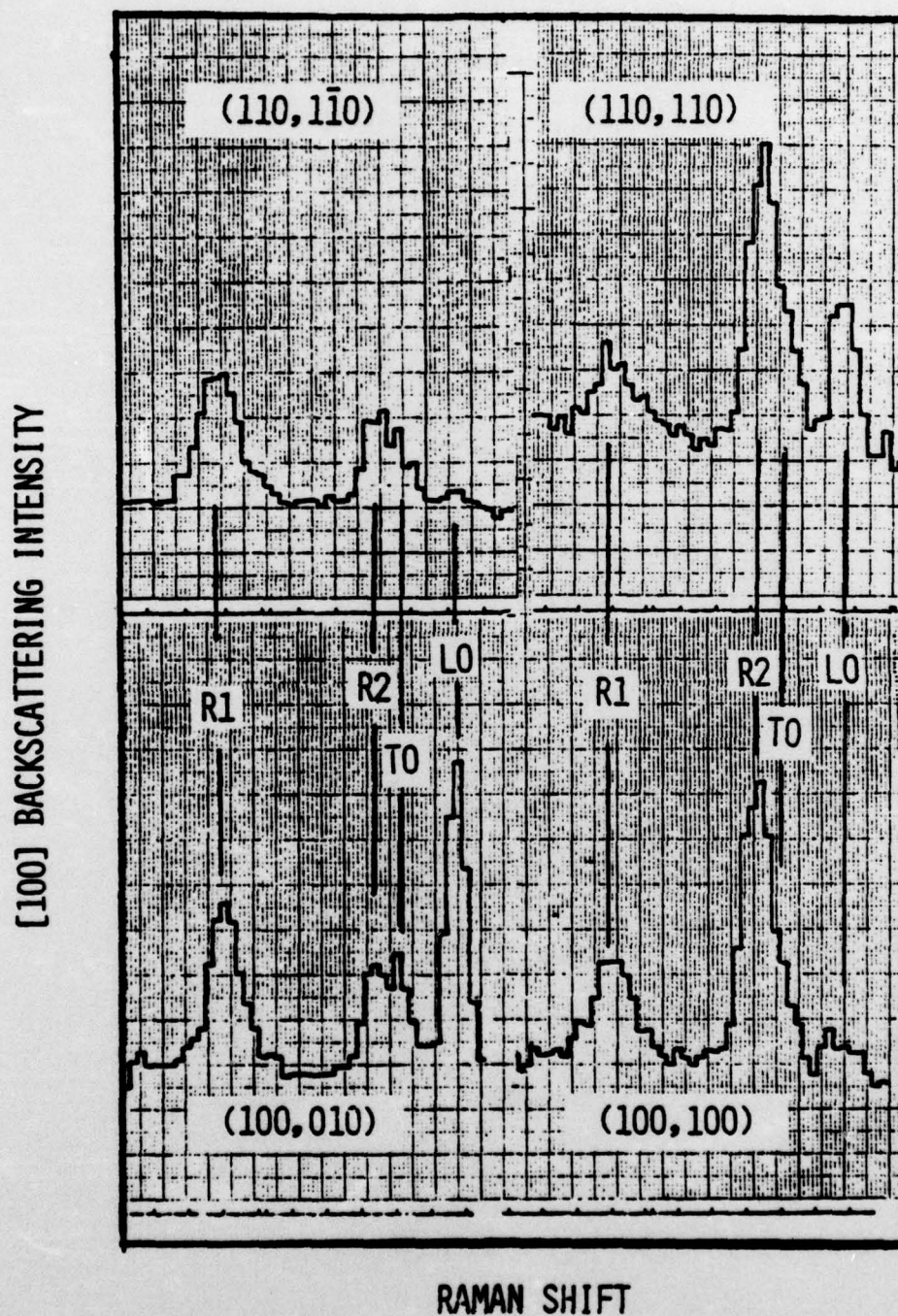


Figure 2

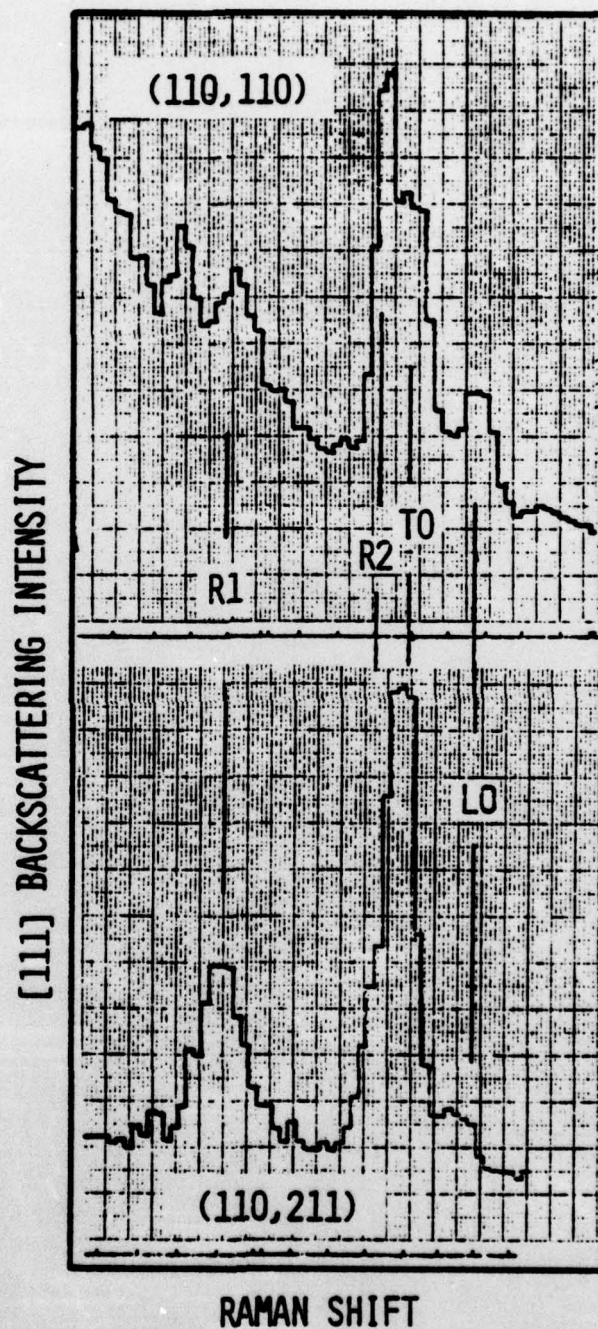


Figure 3